

Application of a Combined Catalyst and Sorbent for Steam Reforming of Methane

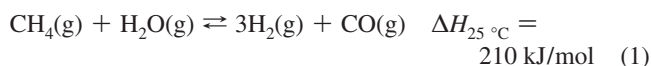
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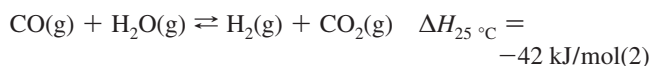
The performance of a combined catalyst and sorbent material designed for reforming hydrocarbons was evaluated by reacting methane with steam at different temperatures and pressures in a reactor packed with the material. The combined material was in the form of small spherical pellets comprised of a sorbent core of lime encased in a porous shell made largely of sintered alumina that supported a nickel catalyst. On the basis of previous research, two shell formulations were included in the study. One shell formulation contained a small quantity of CaO for strengthening of the shells, whereas the other contained a similar quantity of La₂O₃. Reaction testing of the combined catalyst and sorbent over a temperature range of 550–650 °C and a pressure range of 1.0–10.0 atm showed that pellets with either shell formulation were capable of producing H₂ at or near thermodynamic equilibrium levels during a period when CO₂ was being rapidly absorbed by the core material. Limited lifecycle testing of the combined catalyst and sorbent was also conducted at 650 °C and 1.0 atm over 10 cycles of H₂ production and sorbent regeneration. A product stream with 98 mol % H₂ (dry basis) was produced during the rapid CO₂ absorption period of each cycle. However, the length of this period declined with each cycle.

Introduction

Traditionally, methane (CH₄) has been reformed to produce hydrogen by a complex multistep process involving several stages conducted at different temperatures with different catalysts.¹ First, the CH₄ is reacted with steam over a Ni catalyst at 800–870 °C to yield hydrogen and carbon monoxide (CO) via the reforming reaction:

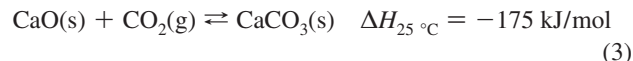


The CO in the mixture is reacted further by applying the water–gas shift reaction shown below in two separate stages.



The first stage is conducted at 350–450 °C with an iron oxide/chromium oxide catalyst, while the second stage is conducted at 200–215 °C with a copper–zinc oxide catalyst. The resulting product mixture is typically scrubbed with a solvent to remove CO₂.

It has been shown that the preceding complex multistep process can be replaced by a much simpler, single-step process operating at an intermediate temperature by the addition of a sorbent that removes CO₂ from the reaction system.^{2–5} Furthermore, it seems that above 500 °C reaction (2) does not require a separate catalyst.⁶ Although different sorbents have been proposed, one of the most promising is CaO, which reacts with CO₂ by the following exothermic reaction:



Because the heat generated by reactions (2) and (3) almost equals that absorbed by reaction (1), little additional heat must be added to or removed from the reaction mixture.

Further simplification of the process has been demonstrated by employing a bed of pellets such that each pellet consists of a sorbent core encased in a strong, porous shell that serves as a catalyst support.^{7,8} The utility of this approach has been demonstrated on a laboratory scale by using spherical pellets with cores made of powdered limestone and with shells made largely of porous alumina impregnated with a Ni catalyst. Initially, the shell material was composed largely of powdered α -Al₂O₃ having a relatively small surface area together with some powdered limestone so that after calcination a binding calcium aluminate phase would be formed. It was shown subsequently that the activity of the catalyst could be improved by replacing a portion of α -Al₂O₃ with higher surface area amorphous Al₂O₃.⁷ More recently, it was discovered that the catalyst activity could be improved further by avoiding the slight sulfur contamination that had occurred inadvertently in the earlier work.⁹ The recent work also indicated that the strength of the shell material could be increased by replacing CaO with La₂O₃.

As part of the continuing development effort, the work reported below extends the application of the combined catalyst and sorbent to CH₄ reforming over a much wider range of temperature and pressure than that previously reported. Furthermore, the work compares the process performance of pellets with lanthanum-containing shells to pellets with calcium-containing shells. In addition, the results of limited lifecycle performance tests of the two materials are reported.

Thermodynamic Analysis

A detailed thermodynamic analysis of the reaction system comprised of the three chemical reactions listed above is

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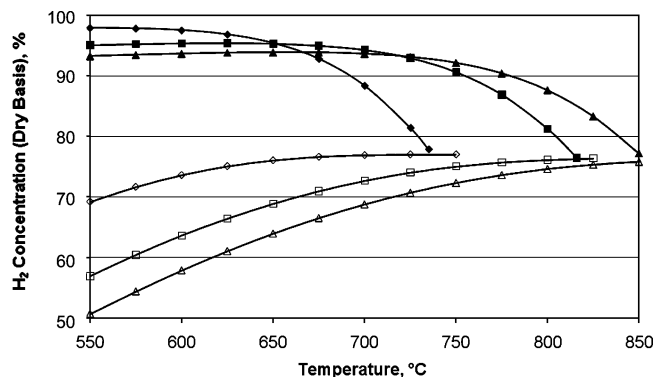


Figure 1. Equilibrium H_2 concentrations on a dry basis for a system supplied with 1.0 mol of CH_4 and 3.0 mol of steam. The closed symbols are with CO_2 absorption, and the open symbols are without CO_2 absorption at 1 atm (\diamond), 5 atm (\square), and 10 atm (\triangle).

revealing. For the system supplied initially with 1.0 mol of CH_4 and 3.0 mol of H_2O in chemical equilibrium, the resulting H_2 concentration is indicated in Figure 1, which is based on published reaction equilibrium constants.^{10,11} Two cases are illustrated. In one case, an active CaO sorbent is present, whereas in a second case, no CaO is present, which would be representative of a fully loaded sorbent. It can be seen that the H_2 concentration is strongly dependent on both the system temperature and pressure and the presence of CaO. By having CaO present to absorb CO_2 , a much larger H_2 concentration can be obtained over a wide range of temperature and pressure. Furthermore, the relative effects of changes in pressure depend on both the temperature and the presence or absence of CaO.

The shapes of the curves in Figure 1 reflect the endothermic/exothermic balance among the three reactions. At lower temperatures where all three reactions play a major role, the H_2 concentration is virtually independent of the temperature because the heats of reaction are balanced. However, at higher temperatures, the two exothermic reactions play an increasingly important role causing the H_2 concentration to decline. When an active sorbent is not present, the shape of the curve is determined by the interplay of reactions (1) and (2). At lower temperatures, the increasing H_2 concentration reflects the endothermic nature of the dominant reaction, or reaction (1). At higher temperatures, exothermic reaction (2) plays a greater role, causing an increase in the temperature to have less and less effect. The points where the two sets of curves intersect correspond to temperatures where the sorbent no longer has a role to play even if present. In other words, at each of these intersections, the partial pressure of CO_2 is in balance with reaction (3).

Further insight is gained from the effects of temperature and pressure on the calculated equilibrium conversions of CH_4 and CO for the two cases based on the presence or absence of CaO. Figure 2 shows that both conversions benefit by the presence of the sorbent over wide ranges of temperature and pressure.

Although these thermodynamic principles have been recognized for a long time, no attempt seems to have been made to conduct all three reactions within the same material until the initial phase of the present project was undertaken.^{7,8}

Experimental Methods and Materials

Materials. The cores of the core-in-shell pellets were made of Microna 3 limestone that had a median particle size of 3.2 μm and a $CaCO_3$ content in excess of 97 wt %. The limestone was supplied by Columbia River Carbonates. The shells were

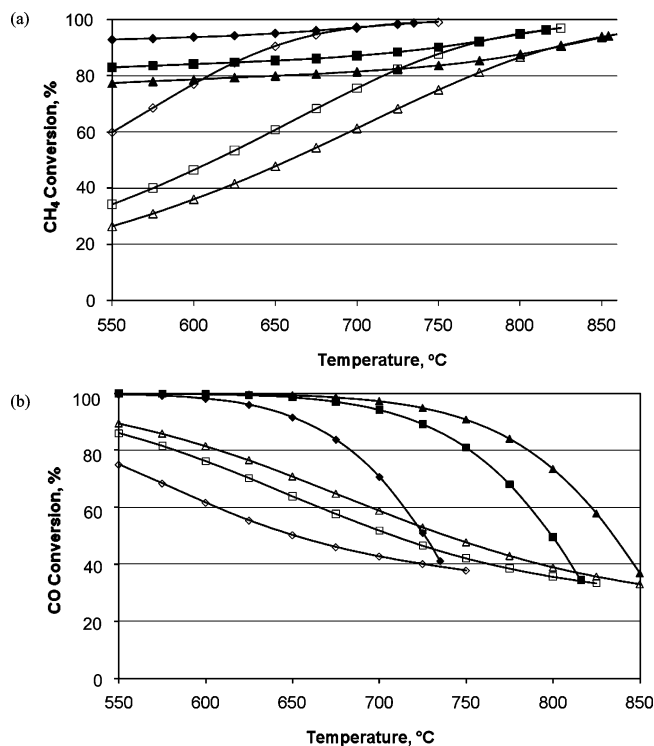


Figure 2. Equilibrium conversions of (a) CH_4 and (b) CO for a system supplied with 1 mol of CH_4 and 3 mol of H_2O . The closed symbols are with CO_2 absorption, and the open symbols are without CO_2 absorption at 1 atm (\diamond), 5 atm (\square), and 10 atm (\triangle).

largely made of Al_2O_3 prepared by combining three different forms of the material. One of these was an amorphous form designated as DD-290 by Engelhard, the supplier. This material had a median particle size of 9.8 μm and a surface area of 275 m^2/g . The other two forms represented different particle sizes of $\alpha-Al_2O_3$ supplied by Almatiss. One of these, designated as T-64, had a median particle size of 8.65 μm and a surface area of less than 1.0 m^2/g . The other, designated as A-16SG, had a median particle size of 0.48 μm and a surface area of 8.2 m^2/g according to the supplier.

Preparation Method. Spherical core-in-shell pellets were prepared by a pan-rolling procedure employing a rotating conical drum pelletizer that had a maximum diameter of 25 cm and could be operated at various speeds. The cores were prepared first by placing Microna 3 limestone powder in the rotating drum and spraying it with water intermittently so that it balled up as the drum revolved at 30 rpm. Pellet cores were built up in this way until about 20 g of pellets ranging between 5 and 6 mesh or between 3.96 and 3.35 mm in diameter was produced. The cores were then hardened by operating the drum at the following speeds for the indicated times: 10 rpm for 10 min, 30 rpm for 20 min, 60 rpm for 30 min, and 90 rpm for 30 min.

The cores were subsequently coated with a shell formulation in powder form by using the same pelletizer. As the prepared cores rolled and tumbled in the pelletizer, the shell powder was added gradually while the pellets were sprayed intermittently with deionized water. As the process continued, the coating of the shell material increased in thickness until the pellets were between 4 and 5 mesh (between 3.96 and 4.76 mm) in diameter. The core-in-shell pellets were subsequently hardened by using the same procedure as that described above for the cores.

Two different shell formulations were employed for coating of the pellet cores, although each was composed largely of powdered alumina having the following composition: 30 wt %

DD-290, 30 wt % T-64, and 40 wt % A-16SG. The first formulation also contained sufficient Microna 3 limestone powder to provide a final mixture with 10 wt % limestone. The materials were readily mixed by employing a small plastic drum that was alternately rolled and shaken. The second formulation contained sufficient lanthanum nitrate to provide a mixture with 92.3 wt % Al_2O_3 and 7.7 wt % La_2O_3 when calcined. It was prepared by dissolving lanthanum nitrate in tetrahydrofuran (THF), which was then mixed with the alumina in a mortar. By control of the quantity of solvent, a relatively thick paste was prepared and partially dried at room temperature and then at 100 °C for 4–5 h. The dried material was ground subsequently with a mortar and pestle. Either of these shell formulations could be applied to the pellet cores as described above.

After the core-in-shell pellets had been prepared with one of the shell formulations, they were calcined at 900 °C for 3 h to strengthen the shells. The calcined pellets were recarbonated with flowing CO_2 at 650 °C and then impregnated twice with nickel nitrate in THF. After each impregnation, the pellets were heated to 500 °C to decompose the nickel nitrate. The gain in weight of the pellets corresponded to an added Ni content of 6 wt %. Prior to reaction testing, the NiO was reduced in situ to form an active Ni metal catalyst by raising the catalyst bed temperature to 550 °C and passing H_2 through the bed. The catalyst prepared by this procedure was highly active and could be used directly for reforming CH_4 .

Performance Testing. Core-in-shell pellets with different shell formulations and loaded with the Ni catalyst were tested in a fixed-bed reactor by reforming CH_4 with steam at different temperatures, pressures, and feed rates. For this purpose, a stainless steel reactor having an inside diameter of 1.58 cm was packed with the core-in-shell pellets interspersed with smaller (1.3-mm-diameter) SiC pellets to reduce channeling and to improve heat transfer. A 10.5 cm bed depth of the active material was employed for runs made at lower pressures (1–5 atm), while a bed depth of 21 cm was used for runs made at 10 atm. A 10-cm-deep layer of extruded SiC pellets was placed above the catalyst bed to mix and preheat the reactants. A quantity of SiC pellets was also placed below the catalyst pellets. A thermocouple was placed in the middle of the catalyst bed to record the temperature.

The fixed-bed reactor could be supplied with CH_4 , CO , H_2 , H_2O , or Ar individually or in appropriate mixtures. H_2O was always supplied as steam generated in a preheater, where deionized water was vaporized. The flow of feedwater was controlled by a Lab Alliance series I HPLC metering pump. Mass flow controllers made by Brooks Instruments were used to control the flow rate of CH_4 , CO , or other gases.

For tests of CH_4 reforming, CH_4 and steam were mixed in the preheater and then passed through heated stainless steel tubing to the heated fixed-bed reactor. After passing through the reactor, the gas mixture was cooled to condense unreacted steam and then vented through a line having a back-pressure regulator to maintain the required system pressure. A bypass line was provided around the reactor for use before the start of a test run. Reactants could be fed through the bypass line at the appropriate flow rate and pressure for the particular conditions being tested, which ensured that a well-mixed, steady flow of reactants could be introduced into the fixed-bed reactor at the beginning of a performance test.

Before the start of a test run, the bed of core-in-shell pellets was heated to 850 °C to ensure that the sorbent was fully regenerated. During this step, steam and CH_4 in a 3:1 mole ratio were passed through the bed at a flow rate of 2.41 mmol/min

for 1.0–1.5 h to regenerate the sorbent while maintaining reducing conditions to prevent any possible oxidation of the Ni catalyst. After this step was completed, the flow of CH_4 and steam was diverted around the reactor through the bypass, while the reactor was cooled to the required temperature for the test run. During this cooling period, no gas was passed through the reactor when it was to be used for a test conducted at 1.0 atm. However, when it was to be used at higher pressures, Ar at a rate of 3.08 mmol/min was supplied to the reactor to pressurize the system. The flow of Ar was continued until other preparations had been completed. At this point, an appropriate flow rate of CH_4 and steam was established through the bypass line. At elevated pressures, the reactants were then passed through the bypass line for at least 15 min to ensure that a steady stream of reactants of the required composition would be supplied to the fixed-bed reactor. The Ar flow was stopped just before introduction of the reactant mixture into the fixed bed.

As the test run proceeded, samples of the reactor effluent were periodically drawn with gastight syringes, and the effluent gas was analyzed with an SRI 8610C gas chromatograph (GC) equipped with a thermal conductivity detector and a flame ionization detector. The samples were analyzed, and the concentrations of H_2 , CO , CO_2 , and CH_4 were normalized to 100%. The gas concentrations reported are the average of several samples drawn during reaction testing at a given temperature and pressure.

Lifecycle Testing. For lifecycle testing of the core-in-shell pellets, the reactor was loaded as described above. The Ni catalyst was reduced initially at 550 °C and 1.0 atm by passing H_2 through the reactor at a rate of 1.3 mmol/min for 4 h. The bed temperature was then increased to 650 °C for a series of lifecycle tests. One cycle consisted of the passing of a reactant stream through the bed of pellets at this temperature for 155 min to demonstrate CH_4 reforming with CO_2 absorption followed by sorbent regeneration at 850 °C. The sorbent was considered regenerated when the CO_2 concentration was stabilized, which usually required 1.0–1.5 h. Throughout the cycle, CH_4 and steam were supplied in a 1:3 mole ratio at a total flow rate of 2.41 mmol/min. Therefore, reducing conditions were maintained throughout the cycle so that the Ni catalyst remained reduced. Also throughout the cycle, samples of the reactor effluent were drawn at 10 min intervals for analysis.

At the end of each cycle, the reactant stream was diverted through the bypass line and around the reactor, while it was cooled from 850 to 650 °C at a rate of 10 °C/min. Once the reactor temperature reached 650 °C, the reactant stream was returned to the reactor and a new cycle began. Because of the time-consuming nature of each cycle, lifecycle testing was limited to 10 cycles for each sample of pellets. However, the 10th cycle was interrupted before regeneration of the sorbent so that it remained in the more stable CaCO_3 form for further evaluation.

If a test had to be interrupted, it was stopped at the end of a H_2 production period so that the pellet cores were left in the CaCO_3 form. During such pauses, Ar was passed through the reactor at 0.44 mmol/min. In addition, the temperature was left at 650 °C to limit the amount of thermal stress experienced by the core-in-shell pellets.

Experimental Results and Discussion

To evaluate the performance characteristics of the core-in-shell pellets with a Ni catalyst, a series of CH_4 reforming test runs was conducted with the material at different temperatures and pressures by employing a fixed-bed reactor loaded with the

Table 1. Summary of Experimental Conditions Employed for the Testing of Core-in-Shell Pellets by Reforming CH₄ with a 3:1 Mole Ratio of Steam to CH₄ in a Fixed-Bed Reactor

bed mass, g	bed volume, cm ³	temp, °C	pressure, atm	feed rate, mmol/min	θ_F , s
13.7	13.3	550	1	2.41	4.90
13.7	13.3	600	1	2.41	4.62
13.7	13.3	600	3	7.23	4.62
13.7	13.3	600	5	12.05	4.60
27.4	26.6	600	10	24.10	9.25
13.7	13.3	650	1	2.41	4.37
13.7	13.3	650	3	7.23	4.37
13.7	13.3	650	5	12.05	4.36
27.4	26.6	650	10	24.10	8.75

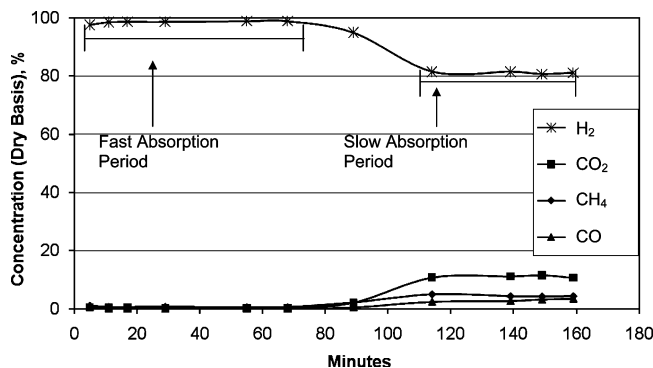
Table 2. Calculated Equilibrium Gas Concentrations for the Test Conditions Listed in Table 1 with a 3:1 Mole Ratio of Steam to CH₄

temp, °C	pressure, atm	CO ₂ absorption	concentration (dry basis), %			
			CH ₄	CO	CO ₂	H ₂
550	1	with	1.9	0.1	0.1	97.9
		without	12.4	4.6	13.8	69.2
600	1	with	1.6	0.5	0.4	97.5
		without	6.0	7.8	12.5	73.6
600	3	with	3.4	0.1	0.1	96.3
		without	14.5	5.1	13.0	67.4
600	5	with	4.5	0.1	0.1	95.4
		without	19.5	4.0	12.9	63.6
600	10	with	6.3	0.0	0.0	93.6
		without	27.0	2.8	12.3	57.9
650	1	with	1.3	2.0	1.3	95.4
		without	2.3	10.8	10.9	76.0
650	3	with	3.0	0.7	0.4	95.9
		without	8.1	8.2	11.8	71.9
650	5	with	4.1	0.3	0.3	95.3
		without	12.2	6.8	12.1	68.9
650	10	with	5.8	0.1	0.1	93.9
		without	18.8	5.1	12.2	63.9

material. These runs were also conducted to compare two different shell formulations made largely of Al₂O₃ but also containing small amounts of either CaO or La₂O₃ and to determine the limited lifecycle performance of the two materials.

The experimental conditions employed for the series of test runs are indicated in Table 1. For the runs conducted at pressures between 1 and 5 atm, a constant mass of pellets was used, whereas for runs conducted at 10 atm, the mass was doubled so that an adequate amount of sorbent was present. Also, for the runs conducted between 1 and 5 atm, the feed rate was increased for the higher pressure runs to keep the apparent reactor space time, θ_F , nearly constant. The apparent space time was taken to be the ratio of the empty reactor volume occupied by the catalyst bed to the volumetric feed rate based on reactor inlet conditions. However, for the runs conducted at 10 atm, it became necessary to double the space time as well as the volume of the catalyst bed to ensure a sufficient sorbent capacity.

For the experimental conditions listed in Table 1, it proved instructive to calculate the equilibrium conversion that could be achieved by steam-CH₄ reforming for the conditions given in this table. Two cases were considered. The first case assumed that CO₂ generated by the reactions of steam and CH₄ and steam and CO would be absorbed by the reaction of CO₂ and CaO under equilibrium conditions. The second case assumed that no CO₂ would be absorbed because the sorbent was fully loaded. On the basis of these equilibrium conversions, the corresponding gas compositions were calculated, and the results are given in Table 2. These results show that, with an active CaO sorbent present, the equilibrium concentration of H₂ would range from 93.6 to 97.9 mol % for the listed conditions. Without the CaO

**Figure 3.** Gas concentrations observed in the reactor effluent during fixed-bed reactor testing of a fresh batch of core-in-shell pellets with limestone added to the shell formulation and impregnated with Ni. Testing was conducted at 600 °C and 1.0 atm.

sorbent, the maximum H₂ concentration attainable would be considerably smaller. Furthermore, without the sorbent, the concentration of H₂ would decrease rapidly with increasing system pressure. Consequently, for systems operating at higher pressures, the role played by the sorbent became even more important.

Performance Tests at Atmospheric Pressure. The performance evaluation of the core-in-shell pellets with improved shell compositions and impregnated with a Ni catalyst was initiated by first conducting a series of runs at atmospheric pressure using the conditions shown in Table 1.

The results of a typical steam-CH₄ reforming test with fresh core-in-shell pellets conducted with a 3:1 mole ratio of steam to CH₄ at 600 °C and 1.0 atm are presented in Figure 3. During the initial 70 min of the test, most of the CH₄ was converted and virtually all of the CO₂ was absorbed, resulting in a high H₂ product concentration. This period will be referred to as the “fast absorption” period. As time progressed, the CaO sorbent was gradually converted to CaCO₃ and the rate of CO₂ absorption slowed significantly. Eventually, the product gas composition became nearly constant, and this period will be referred to as the “slow (CO₂) absorption” period. An analysis of the product gas observed during the slow absorption period showed that the steam-CH₄ reforming and water-gas shift reactions could not solely account for the observed reactor effluent composition. On the other hand, when CO₂ absorption was taken into account, the conversions obtained were consistent. Thus, the slow absorption of CO₂ by the CaO sorbent appeared to be taking place even after an extended time.

During the slow absorption period, the H₂ concentration was significantly lower than that during the fast absorption period, whereas the CO, CO₂, and CH₄ concentrations were higher. The slow absorption period was characterized by a partially loaded CaO sorbent that continued to absorb CO₂ through a diffusion-limited reaction. The phenomenon of CaO slowly absorbing CO₂ after an initial rapid, kinetically controlled period is a well-known property of CaO-based sorbents.^{12,13} A comparison of the gas concentrations observed during the slow absorption period with those recorded in Table 2 for the same temperature and pressure without CO₂ absorption also indicated that the system had not yet reached an equilibrium state. For example, the observed H₂ concentration of over 80 mol % was significantly greater than the equilibrium value of 73.6 mol % reported in Table 2 for 600 °C and 1.0 atm and without CO₂ absorption.

To gain some appreciation of how much more CO₂ would have been absorbed if the test had been extended for a very long time, another run was conducted using similar conditions

Table 3. Average Product Gas Concentrations Observed during the Three Periods of Operation^a

operating period	gas concentration (dry basis), mol %			
	CH ₄	CO	CO ₂	H ₂
fast absorption	0.9	0.9	0.7	97.4
slow absorption	2.3	4.7	12.1	80.9
steady state	3.0	5.6	14.4	77.0

^a Run conditions: 3:1 mole ratio of H₂O to CH₄; 2.41 mmol/min; 650 °C, 1.0 atm.

Table 4. Reactor Effluent Composition During the Testing of Core-in-Shell Pellets with a Ni Catalyst and Different Shell Formulations^a

test conditions		concentration (dry basis), mol %							
		shell with limestone				shell with lanthanum			
temp, °C	absorption period	CH ₄	CO	CO ₂	H ₂	CH ₄	CO	CO ₂	H ₂
550	fast	1.7	0.2	0.2	97.9	1.4	0.1	0.4	98.1
	slow	10.4	2.2	14.3	73.1	10.7	1.6	12.3	75.4
600	fast	0.8	0.1	0.4	98.7	1.1	0.1	0.6	98.1
	slow	5.0	2.8	12.8	79.4	4.9	3.2	12.8	79.1
650	fast	0.8	0.5	0.8	98.0	0.7	0.4	0.5	98.5
	slow	2.0	5.7	12.3	80.1	1.7	5.0	12.3	81.0

^a Testing was conducted at 1.0 atm.

except that the temperature was increased to 650 °C and the run was continued for 875 min. The results were generally similar to those shown in Figure 3. The fast absorption period lasted for approximately 100 min and the slow absorption period for another 100–150 min. After that, the concentration of CO₂ increased very gradually for another 300–400 min before reaching an apparent steady state. The average product gas concentrations during these three periods of operation are shown in Table 3. The gas composition shown for the steady-state absorption period is an average of the values recorded over the final 260 min of the run. The steady-state composition seems to represent the gas concentrations that would have been obtained without a sorbent present. A comparison of this composition with that recorded during the slow absorption period shows that the differences are relatively small. Also, a comparison of the results in Table 3 with the equilibrium composition listed in Table 2 indicates a relatively good agreement between the gas composition noted during the fast absorption period and the equilibrium composition with CO₂ absorption. In addition, the H₂ concentration of 77 mol % and the CH₄ concentration of 3.0 mol % observed during the steady-state period agree well with the corresponding equilibrium values of 76 mol % H₂ and 2.3 mol % CH₄ in Table 2. On the other hand, this agreement did not extend to the CO and CO₂ components of the gas mixture.

Additional runs were conducted at 1.0 atm with core-in-shell pellets to compare the two shell formulations and to gain a better understanding of the effect of the temperature. The reactor effluent composition produced during each of these runs is presented in Table 4 for both the fast and slow CO₂ absorption periods of operation. A comparison of the effluent compositions for the two different shell formulations showed them to be very similar and consistent for both CO₂ absorption periods at all three temperature levels. For the fast CO₂ absorption period, a change in the temperature over the 550–650 °C range had little effect on the effluent composition that consistently included 98 mol % H₂. For the slow absorption period, the H₂ content of the effluent was smaller, but it increased from about 74 mol % to over 80 mol % as the temperature rose. These trends reflected similar trends in the calculated equilibrium gas concentrations

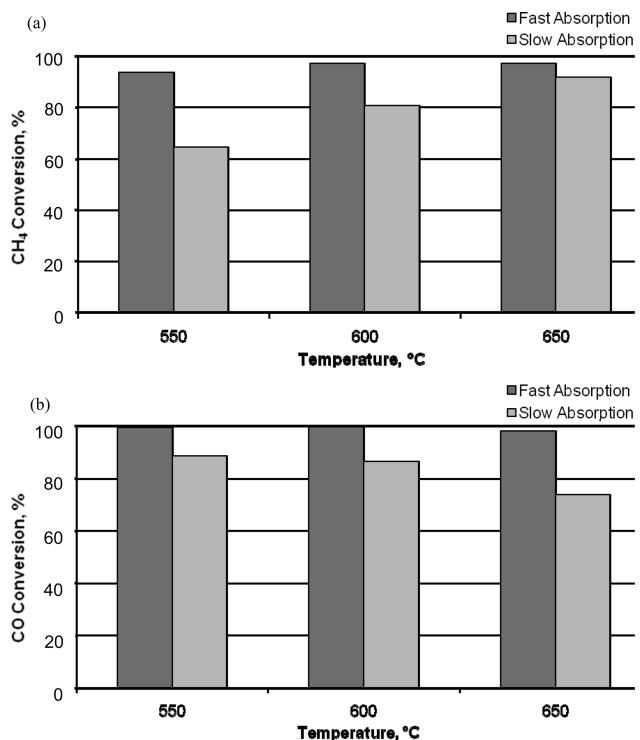


Figure 4. Observed CH₄ and CO conversions recorded during fixed-bed reactor testing of core-in-shell pellets at 1.0 atm with a Ni catalyst and with limestone in the shell formulation.

presented in Figure 1 and Table 2. As expected, there was a relatively good agreement between the test results for the fast CO₂ absorption period and the calculated equilibrium values when CO₂ was absorbed. Therefore, the process appeared to be controlled by thermodynamic equilibrium. For the slow CO₂ absorption period, the process seemed to be controlled by the rate of CO₂ absorption because the reactor effluent had a lower concentration of CH₄ and a higher concentration of H₂ than would have resulted without CO₂ absorption under equilibrium conditions, as indicated by Table 2.

The gas concentrations in Table 4 were used to determine the CH₄ and CO conversions for both pellet formulations. Because the results were so similar, only conversions representing pellets with the limestone shell formulation are shown in Figure 4. A comparison of these conversions with the equilibrium values in Figure 2 shows that for the fast CO₂ absorption period there is a good agreement between the two sets of values at 1.0 atm. For the slow CO₂ absorption period, the observed CH₄ conversions tend to agree with the equilibrium values without CO₂ absorption shown in Figure 2a. However, for this period, the observed CO conversions were much greater than the equilibrium values without CO₂ absorption because some CO₂ was actually absorbed albeit slowly.

Performance Testing at Elevated Pressures. The performance of core-in-shell pellets was also evaluated at absolute pressures of 3.0, 5.0, and 10.0 atm and at temperatures of 600 and 650 °C. Core-in-shell pellets with limestone or with lanthanum added to the shell formulation were tested separately. A steam-to-CH₄ feed ratio of 3:1 was employed throughout the series of tests, while the total molar flow rate of the feed was increased in proportion to the pressure. Thus, as indicated in Table 1, the space time of the reactants passing through the bed remained the same at 1.0, 3.0, and 5.0 atm. At 10.0 atm, the increased flow rate necessitated doubling of the mass of core-in-shell pellets so that adequate sorbent was present for the fast absorption period. Doubling the mass of pellets also

Table 5. Reactor Effluent Concentrations during Testing of the Core-in-Shell Pellets with a Ni Catalyst and Different Shell Formulations

expt. conditions			concentration (dry basis), mol %							
			shell with limestone				shell with lanthanum			
temp, °C	pressure, atm	absorption period	CH ₄	CO	CO ₂	H ₂	CH ₄	CO	CO ₂	H ₂
600	3	fast	2.5	0.1	0.3	97.2	2.2	0.1	0.2	97.5
		slow	14.5	3.5	12.2	69.9	15.3	2.3	11.9	70.5
	5	fast	3.1	0.1	0.2	96.6	3.5	0.1	0.2	96.2
		slow	19.0	2.5	12.3	66.3	17.9	2.0	11.6	66.7
	10	fast	6.0	0.0 ^a	<0.1	93.8	5.1	0.0 ^a	<0.1	94.9
		slow	41.8	0.7	9.2	48.2	39.9	0.9	8.6	50.6
650	3	fast	2.0	0.2	0.2	97.6	1.7	0.2	0.8	97.4
		slow	8.9	4.9	11.7	74.5	8.4	4.5	11.9	75.2
	5	fast	2.9	0.1	0.6	96.4	3.0	0.2	0.6	96.2
		slow	11.7	4.0	12.3	72.0	11.7	3.7	12.0	72.6
	10	fast	4.8	0.0 ^a	<0.1	95.1	5.3	0.0 ^a	<0.1	94.7
		slow	31.0	2.8	11.1	55.0	30.5	1.3	11.0	57.2

^a Below detection limits.

doubled the length of the catalyst bed, effectively doubling the space time of the gas passing through the bed.

The reactor effluent concentrations observed during operation of the reactor filled with pellets made with either shell formulation are shown in Table 5. Again, it can be seen that the results obtained with the two different shell formulations are quite similar. Table 5 shows that during the fast CO₂ absorption period H₂ in high concentrations was produced at all pressures and temperatures. Also, unreacted CH₄ was the principle impurity while CO and CO₂ were present in very low concentrations. At 10.0 atm, the concentration of CO₂ was less than 0.1 mol % and the concentration of CO was below the detection limits of the GC. Thus, increasing the system pressure during the fast absorption period diminished CH₄ conversion, in agreement with Figure 2a, and also resulted in lower concentrations of H₂, CO, and CO₂.

The gas concentrations in Table 5 were used to determine the CH₄ and CO conversions for both pellet formulations at 3.0, 5.0, and 10.0 atm. Again, because the results were so similar, only the conversions representing pellets with the limestone shell formulation are presented in Figure 5. The CH₄ conversions for the fast absorption period are approximately equal to the thermodynamic equilibrium levels shown in Figure 2a. Additionally, for tests conducted at 3 and 5 atm, the observed concentrations in Table 5 for the fast absorption period are comparable to the calculated equilibrium concentrations in Table 2. In both Figures 2 and 5a, it can be seen that for a given pressure CH₄ conversion does not have a strong dependence on the temperature during the fast absorption period. This result is probably due to the balance between the endothermic and exothermic heats of reaction for the three reactions involved.

It can also be seen in Figure 5a that an increase in the pressure reduced CH₄ conversion, which was expected because of the change in the number of moles of gas because all three reactions took place during the fast absorption period. A comparison of the actual CH₄ conversions for the slow absorption period in Figure 5 with the equilibrium values appearing in Figure 2 for no CO₂ absorption shows a good agreement at 5 atm but not at 10.0 atm, where the actual CH₄ conversions were considerably lower than the equilibrium values. A lower conversion at 10.0 atm during the slow absorption period could have been due to a temperature gradient across the bed of pellets caused by the highly endothermic reforming reaction. Alternatively, the reaction kinetics could also have been affected by the higher pressure. Of greater interest were the effects of the temperature and pressure on the CO conversion during the slow absorption period, where at any specific temperature and pressure the actual

CO conversion was always greater than the equilibrium conversion that did not account for CO₂ absorption. Therefore, these results further indicate that CO₂ was being absorbed during the slow absorption period.

Lifecycle Testing of Core-in-Shell Pellets with a Ni Catalyst. Limited lifecycle testing of the core-in-shell pellets was conducted to evaluate the performance of the pellets as they were subjected to 10 cycles of H₂ production and subsequent sorbent regeneration at 1.0 atm. Core-in-shell pellets with either the limestone shell formulation or the lanthanum shell formulation were prepared for fixed-bed reactor testing. A fresh batch of 13.7 g of core-in-shell pellets was loaded into the fixed-bed reactor for each test. After an initial reduction of the NiO catalyst to Ni by flowing H₂ at 550 °C, the pellets were ready for the first cycle. The reactor temperature was increased to 650 °C, and steam and CH₄ in a 3:1 mole ratio were fed to the reactor at a rate of 2.41 mmol/min. During this time, a

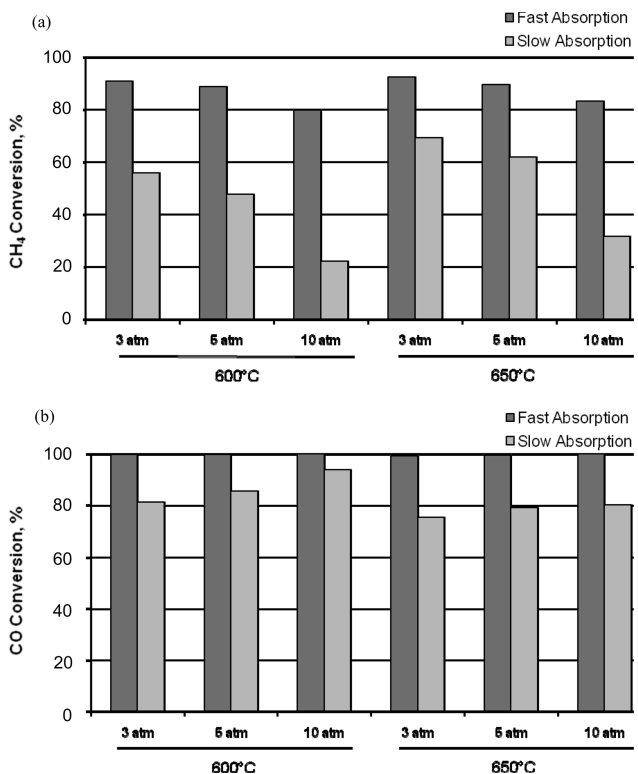


Figure 5. Observed CH₄ and CO conversions recorded during fixed-bed reactor testing at higher pressures of core-in-shell pellets with a Ni catalyst and with limestone in the shell formulation.

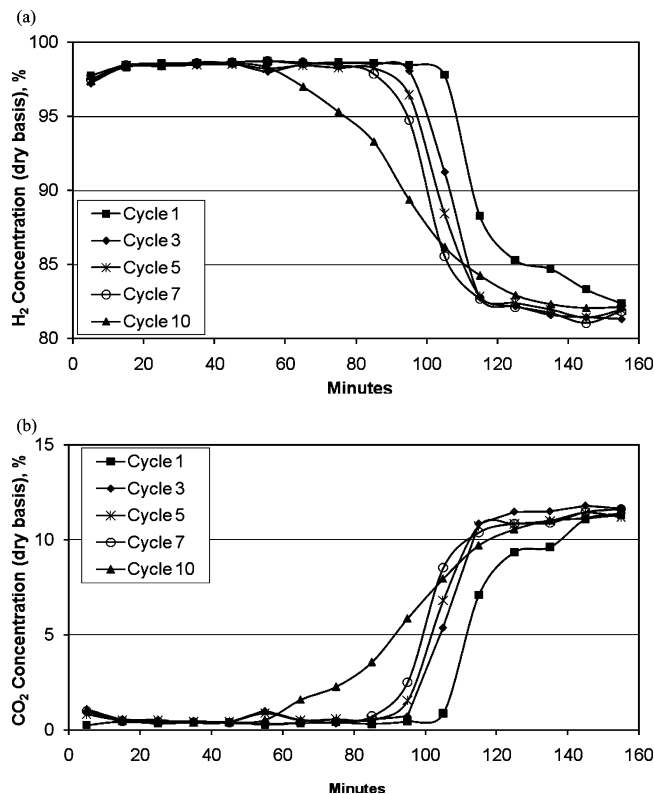


Figure 6. Concentrations of H₂ and CO₂ in the reactor effluent during lifecycle testing of core-in-shell pellets with the limestone shell formulation. Tests were conducted at 1.0 atm and 650 °C during the CH₄ reforming phase shown here.

sample of the reactor effluent was drawn every 10 min for analysis in order to record the reactor response curve. After 155 min, the reactor temperature was raised from 650 to 850 °C at a rate of 10 °C/min while continuing the flow of reactants to regenerate the CaO sorbent. When the CO₂ concentration in the reactor effluent reached a constant level at 850 °C, the sorbent was considered regenerated. During regeneration, the flow of reactants was continued to ensure that the Ni catalyst remained reduced. Regeneration took 1.0–1.5 h at 850 °C. The period of reaction testing for 155 min at 650 °C, followed by the regeneration step at 850 °C, constituted a complete cycle. Each pellet formulation was subjected to 10 cycles. However, the sorbent was not regenerated after the 10th reaction stage at 650 °C, so that it was left in the more stable CaCO₃ form for further evaluation.

Core-in-shell pellets with limestone added to the shell formulation were tested first. As each test cycle proceeded, the concentrations of H₂ and CO₂ in the reactor effluent were recorded during the CH₄ reforming phase (see parts a and b of Figure 6, respectively). At the beginning of each cycle and for an extended period, CO₂ was rapidly absorbed so the concentration of CO₂ was only 0.8 mol % in the reactor effluent. During this period, the rates of the steam–CH₄ reforming reaction, water–gas shift reaction, and reaction between CaO and CO₂ were sufficiently rapid to produce H₂ in 98 mol % concentration. Eventually, as time progressed, the rate of CO₂ absorption by CaO slowed so its concentration rose to about 12 mol %, while the H₂ concentration fell to 81–82 mol %. As the number of cycles increased, the time that H₂ was produced in 98 mol % concentration also decreased from approximately 100 min for the first cycle to 50 min for the last cycle. Also, Figure 6b indicates that as the number of cycles increased the period during which CO₂ was rapidly absorbed decreased from over 100 min

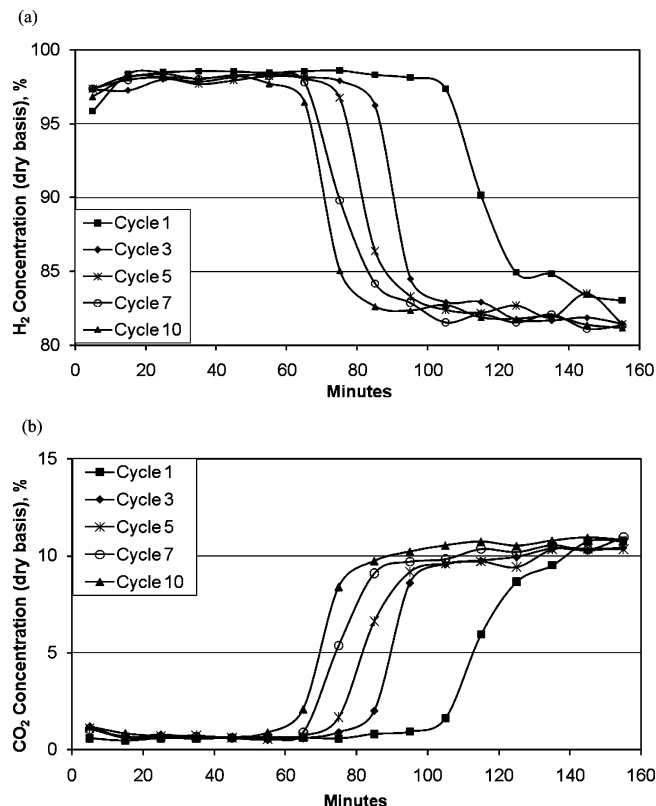


Figure 7. Concentrations of H₂ and CO₂ in the reactor effluent during lifecycle reaction testing of core-in-shell pellets with the lanthanum shell formulation. Tests were conducted at 1.0 atm and 650 °C during the CH₄ reforming phase shown here.

for the first cycle to 50 min for the last cycle. Thus, the amount of CO₂ that was absorbed rapidly diminished as the sorbent absorption capacity decreased. While the length of time that CO₂ was rapidly absorbed decreased as the number of cycles increased, H₂ in high concentration was produced during a portion of each cycle. Thus, more mature samples of combined catalyst and sorbent were still capable of producing H₂ in high concentration, but the length of time that the high concentration of H₂ was produced decreased with each cycle.

For the first seven cycles, the transition time between the rapid and slow CO₂ absorption periods was relatively short. However, the transition time between the 7th and 10th cycles was longer, which could have been due to changes in either the core or shell material. As the number of cycles increased, the CaO cores may have become denser because of the expansion and contraction associated with the change in the molar volume as the sorbent was transformed between CaO and CaCO₃. Also, because the melting point of CaCO₃ is 1330 °C,¹⁴ it would have a Tamman temperature of 665 °C. Therefore, enhanced sintering of the core could have taken place at 650 °C when the core was in the form of CaCO₃ or before the core was completely regenerated at 850 °C. Densification and sintering of the core would tend to reduce the rate of diffusion of CO₂ into the core and thereby reduce its overall rate of absorption.

The performance of core-in-shell pellets with lanthanum added to the shell formulation was also investigated over 10 cycles of reaction and sorbent regeneration. Figure 7 shows the concentrations of H₂ and CO₂ observed during lifecycle testing of the pellets. While the results were generally similar to those observed with the previous pellets, there were some important differences that seemed due to the difference in the shell

formulations. In both cases, H₂ in 98 mol % concentration was produced during the initial rapid CO₂ absorption period, followed by the production of H₂ in 82 mol % concentration during the slow CO₂ absorption period. However, after the first cycle, the concentration profiles differed appreciably between shell formulations for the transition from one CO₂ absorption period to the next. Furthermore, this difference appeared to increase as the number of cycles increased. The results suggest that the two materials will need to be tested over many more cycles before a definite conclusion can be reached about their relative performance.

Summary and Conclusions

The performance characteristics of an advanced material designed for the reforming of hydrocarbons were determined by reacting steam and CH₄ in a fixed-bed reactor packed with a pelletized material. Each pellet had a core derived from limestone and a shell made largely of alumina, with a small quantity of either a limestone or a La₂O₃ precursor to strengthen the shell material upon calcination. After the pellets had been calcined at 900 °C and loaded with the Ni catalyst, they were tested in the reactor by conducting a series of test runs at different temperatures and pressures. For these runs, steam and CH₄ were supplied in a 3:1 mole ratio. As the reactor temperature and pressure were varied, the feed rate was changed to maintain a constant space time except for tests conducted at the highest pressure, i.e., 10 atm. For this exception, both the active bed volume and space time had to be doubled to provide sufficient sorbent.

At the start of each absorption test and for a prolonged period of operation, virtually all of CO₂ was absorbed, resulting in an overall rapid rate of reaction. During this fast (CO₂) absorption period, the conversion of CH₄ appeared to be limited by thermodynamic equilibrium. Eventually, as the sorbent became loaded, the rate of CO₂ absorption decreased and appeared to become limited by the rate of diffusion of CO₂ through the partially reacted sorbent, resulting in a slow absorption period. During this period, the results were only slightly better than those for a system in equilibrium without a CO₂ sorbent present. Because the conversion of CH₄ and CO both decreased significantly during the slow absorption period, it is apparent that the absorption of CO₂ played a very important role.

During the fast absorption period, which is of greatest interest, changes in the temperature between 550 and 650 °C had little effect on the conversion of either CH₄ or CO. On the other hand, during this period, an increase in the pressure from 1 to 10 atm caused the conversion of CH₄ to decrease noticeably while having only a slight effect on the conversion of CO. At the highest pressure, CO could no longer be detected. The overall effect of these changes on the product composition was small during the fast absorption period. The concentrations of CH₄ and H₂ were mostly affected so that, as the pressure increased from 1 to 10 atm, the concentration of unreacted CH₄ increased from 1 to 5 mol % (dry basis) and the concentration of H₂ decreased from 98 to 95 mol % (dry basis).

Lifecycle testing of the core-in-shell pellets subjected to 10 cycles of H₂ production and sorbent regeneration at 1.0 atm

and 650 °C consistently produced a product stream with 98 mol % H₂ (dry basis) during the fast absorption period of each cycle. However, the length of the fast absorption period decreased from cycle to cycle, most likely because of changes in the properties of the sorbent.

A comparison of the results achieved with the two different shell formulations showed them to be remarkably similar and quite consistent. Further development and testing will be required to determine whether the substitution of lanthanum for calcium in the pellet shell material offers a distinct advantage such as increased shell strength.

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